

CO₂ Hydrogenation to Alcohols over Highly Dispersed Co/SiO₂ Catalysts Derived from Acetate

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Highly dispersed Co(A)/SiO₂ catalysts were prepared from acetate, and used for CO₂ hydrogenation to alcohols under the reaction conditions of T = 493 K, P = 2.1 MPa, H₂/CO₂ = 3/1, and GHSV = 2000 h⁻¹. Catalytic activity was greatly improved by adding a small amount of Ir to the catalyst, and methanol (ca. 20%) was formed, in contrast with Co(N)/SiO₂ catalyst derived from nitrate. Ethanol selectivity was increased up to 8% by adding Na salt to the Ir/Co(A)/SiO₂ catalyst.

Catalytic hydrogenation is one of the most promising ways of CO₂ fixation from view points of the efficiency and the diversified products.¹ Methanol (MeOH) synthesis by CO₂ hydrogenation has been extensively studied over mainly Cu-based catalysts, and even a bench scale test is now in progress.² On the contrary, only several investigations have been reported on the direct conversion of CO₂ to ethanol (EtOH). Okamoto et al.³ and Inui et al.⁴ developed combined catalyst systems based on K/Fe–Cu–ZnO(–Al₂O₃), respectively, and high STY of EtOH was obtained. The concept of the catalyst design is reported to be the combination of C–C bond formation catalysts and catalysts for oxygenate formation. Rh-based catalysts were reported by Kusama et al.⁵ Rh is known as the typical catalyst species for oxygenate production from synthesis gas (CO/H₂ mixture). The concept of the catalyst design is the modification of the electronic state of Rh, resulting in application to CO₂ hydrogenation. Ru-based homogeneous catalyst system was also reported by Tominaga et al.⁶ The noble metal catalysts are financially limited for wide application in industrial scale.

Cobalt is well known as typical catalyst for Fischer–Tropsch (F–T) synthesis to form hydrocarbons. However, it is reported that some oxygenates are also formed in F–T reaction, when Co is highly dispersed.⁷ The catalysts for CO hydrogenation is generally applicable to CO₂ hydrogenation, too. Thus, Co/SiO₂ catalysts with high-dispersion were prepared from acetate, and

tried to use for CO₂ hydrogenation to oxygenates.

Silica gel (Fuji–Davison #57, 16–32 mesh size, S = 260 m²g⁻¹, V_p = 1.2 cm³g⁻¹, D_p = 18 nm) was impregnated with aqueous solution of cobalt acetate or nitrate by the incipient wetness method to form 5 wt%–Co/SiO₂ catalysts (denoted as Co(A)/SiO₂ and Co(N)/SiO₂, respectively). Alkali and alkaline earth metal (M) acetate were added by co-impregnation. After pre-treatment in H₂ flow at 573 K for 3 h, Ir₄(CO)₁₂ was added to Co–M/SiO₂ by the vapor phase deposition method at 433 K *in vacuo*. After reducing the Ir/Co–M/SiO₂ catalysts at 723 K for 3 h, CO₂ hydrogenation was carried out under reaction conditions of T = 473–508 K, P = 2.1 MPa, H₂/CO₂ = 3/1, GHSV = 2000 h⁻¹. Effluent gas from the fixed bed reactor was analyzed by on-line gas chromatography.

The reaction results at 493 K were summarized in Table 1. The amounts of the additives were Ir/Co/M = 0.13 / 1.0 / 0.67 in atomic ratio. Since almost no deactivation was observed, the results at time-on-stream of t = 4–6 h were listed. The conventional catalyst Co(N)/SiO₂ showed relatively high activity without additives, and the main product was CH₄, as commonly recognized.⁸ In contrast, the catalyst derived from acetate without additives, Co(A)/SiO₂, showed almost negligible activity. The results of XPS and H₂ chemisorption measurement indicated that Co in Co(N)/SiO₂ could be reduced to metallic state, Co⁰, while that Co in Co(A)/SiO₂ was hardly reduced. However, by adding Ir to Co(A)/SiO₂ (Ir/Co = 0.13 in atomic ratio), CO₂ conversion was greatly improved, and MeOH was formed. Since Ir/SiO₂ itself did not show any activity in CO₂ hydrogenation, the improvement is thought to be a synergistic effect between Ir and Co(A)/SiO₂. The TPR result indicated that Ir/Co(A)/SiO₂ was easily reduced as low as 540 K, while that Co(A)/SiO₂ was not reduced below 1070 K. The XPS results showed that %reduction to Co⁰ (or 100 × Co⁰/(Co⁰+Co²⁺)) on Ir/Co(A)/SiO₂ surface was %Co⁰ = 75%, which was almost comparable to Co(N)/SiO₂ surface, %Co⁰ = 73%, as shown in

Table 1. CO₂ hydrogenation over Co-based catalysts^a

Catalyst ^b	CO ₂ conv. / C-%	CH ₄ selec. / C-%	C ₂₋₈ ^c selec. / C-%	CO selec. / C-%	MeOH selec. / C-%	EtOH selec. / C-%
Co(N)/SiO ₂	9.2	93.8	3.4	0.0	2.7	0.1
Co(A)/SiO ₂	0.5	15.0	0.8	67.0	17.1	0.0
Ir/SiO ₂	0.5	9.4	0.5	90.1	0.0	0.0
Ir/Co(A)/SiO ₂	10.0	68.2	1.5	9.6	20.3	0.4
Ir/Co(A)–MgO/SiO ₂	11.9	64.5	2.2	10.9	21.9	0.6
Ir/Co(A)–CaO/SiO ₂	5.4	21.9	0.8	41.0	35.2	1.1
Ir/Co(A)–SrO/SiO ₂	4.7	32.1	0.9	38.7	27.0	1.2
Ir/Co(A)–Li ₂ O/SiO ₂	5.6	49.7	7.1	24.4	16.3	2.5
Ir/Co(A)–Na ₂ O/SiO ₂	7.6	35.7	9.6	38.5	7.8	7.9
Ir/Co(A)–K ₂ O/SiO ₂	7.8	28.5	4.2	55.6	5.6	6.1

^aReaction conditions: T = 493 K, P = 2.1 MPa, H₂/CO₂ = 3/1, GHSV = 2000 h⁻¹. ^bIr / Co / M = 0.13 / 1.0 / 0.67 (in atomic ratio); M = Mg, Ca, Sr, Li, Na, K. ^cC₂₋₈ hydrocarbons.

Table 2. %Co⁰ determined by XPS, and H₂ volume adsorbed

Catalyst	Ir/Co ^a	Na/Co ^a	%Co ⁰	H ₂ ads. / cm ³ g ⁻¹
Co(N)/SiO ₂	-	-	73.1	0.195
Co(A)/SiO ₂	-	-	4.4	0.001
Ir/SiO ₂	-	-	-	0.278
Ir/Co(A)/SiO ₂	0.03	-	22.6	0.156
Ir/Co(A)/SiO ₂	0.07	-	31.0	0.217
Ir/Co(A)/SiO ₂	0.13	-	75.0	0.316
Ir/Co(A)-Na ₂ O/SiO ₂	0.13	0.67	74.9	0.279

^aAtomic ratio. ^b 2 wt%Ir/SiO₂.

Table 2. The similar effects of reduction by Pt and Ru addition have been also reported on Co-based catalysts for F-T synthesis.⁹ However, no XRD peaks were observed on the Co(A)/SiO₂ and Ir/Co(A)/SiO₂ catalysts, implying that the crystallite size of Co metal of these catalysts was smaller than 3 nm. On the other hand, the crystallite size of Co of Co(N)/SiO₂ was estimated at about 6 nm by the XRD line broadening. These results suggest that the highly dispersed Co catalyst is obtained from acetate and activated by adding Ir, and that the high dispersion is responsible for oxygenate selectivity. The effect of the adding amount of Ir to the Co(A)/SiO₂ catalyst was investigated in the range of Ir/Co = 0.03–0.26. Although H₂ adsorption amount was increased with Ir amount, CO₂ conversion and selectivity were slightly affected in the range.

The effect of alkaline earth metal (M) additives on CO₂ hydrogenation was investigated over Ir/Co(A)/SiO₂ catalyst (M/Co = 0.67 in atomic ratio). CO₂ conversion and CH₄ selectivity tended to be decreased, and CO selectivity was increased, with the basicity of alkaline earth metal additives. The highest MeOH selectivity up to 35% was obtained over Ir/Co(A)-CaO/SiO₂ catalyst, which showed moderate selectivity for CH₄ and CO. The catalyst with high hydrogenation activity may show the highest CH₄ selectivity, for CH₄ is the most extremely hydrogenated product. Since CO₂ adsorbed on the catalyst surface is consecutively hydrogenated to CH₄ via CO adsorbed species, CH₄ selectivity is generally traded off with CO selectivity. Thus, CO formation as well as moderate hydrogenation activity may be prerequisite to MeOH formation.

Effects of alkali metal additives were also examined. Methane selectivity was decreased and CO selectivity was increased with the basicity of the additives, in a similar manner as alkaline earth metal additives. In contrast with alkaline earth metal addition, however, selectivity for C₂₊ hydrocarbons increased, and EtOH, instead of MeOH, was formed by adding alkali metal additives. The C–C bond formation of reaction intermediates was presumably promoted by alkali metal addition, resulting in EtOH selectivity. The selectivity was hardly varied in the conversion range of 5–26%. The highest selectivity up to 8% was obtained over Ir/Co(A)-Na₂O/SiO₂ catalyst.

In conclusion, highly dispersed Co(A)/SiO₂ catalyst obtained from acetate was drastically activated by impregnating with Ir, resulting in MeOH formation in CO₂ hydrogenation. By adding alkaline earth and alkali metal salts to Ir/Co(A)/SiO₂ catalysts, the selectivity for MeOH and the selectivity for EtOH

were increased, respectively. Since conversion was increased without significant change in EtOH selectivity at a higher temperature below 523 K, the highest STY of EtOH up to 7.9 g dm⁻³ h⁻¹ was obtained over Ir/Co(A)-Na₂O/SiO₂ catalyst at 508 K.

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